A

RESEARCH PROPOSAL

ON TOPIC

A STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF SOME DIVALENT TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDE IN WATER AND WATER+MONOHYDROXY ALCOHOLS

SUBMITTED

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SUBMITTED BY:
SONIKA SINGH

SUPERVISED BY:
Dr. M.L.PARMAR
Dr.RAMESH THAKUR

FACULTY OF TECHNOLOGY AND SCIENCES
LOVELY PROFESSIONAL UNIVERSITY
PUNJAB

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INTRODUCTION

The study of electrolyte solutions, an area of traditional interest with in physical chemistry, has expanded in several directions during recent years. Of major importance has been the introduction of an increasingly wide range of solvents as reaction media. The thermodynamics of ion-solvent interactions are of fundamental importance to an understanding of the rates and equilibria of reactions involving electrolytes in solutions. The study of thermodynamic properties of the electrolytic solutions provides an opportunity for extending the range of properties from which the structure of electrolyte solution can be inferred.

It has been realized that ion-solvation can be better understood in mixed solvents than in pure solvents, because the dielectric constant can be varied to a desired value in mixed solvents. The ion-ion and ion-solvent interactions play an important role[1]in the solution chemistry. For the study of ion-solvent interactions, water has been used extensively as a component in mixed solvents, due to its easy availability and high dielectric constant. If the nature of water can be modified by a co-solvent in such a way that the electrostatic effects, arising from dielectric constant, remain almost the same, then the chemical effects of the co-solvent should play an important role in influencing the ion-ion interactions.

Moreover, mixed binary aqueous solvent systems behave in an unexpected manner as compared to the behaviour of non-aqueous systems. These observations have given a new impetus to the detailed study of structure of binary aqueous mixtures. The information drawn from these studies of thermodynamic properties have been related to structural aspect of the solvent in terms of the ion-solvent and solvent-solvent interactions and structure making/breaking capacity of various electrolytes.

The thermodynamic properties are of course interesting in themselves, but their ultimate importance lies in what they can tell us about chemical equilibrium. Likewise, the transport properties are fascinating studies in themselves, but their industrial and practical values lie in the way they control important reaction rates, including the most important reaction of all the human thought process.

Most of the recent interest in the solution properties of transition metal ions arose in biology and particularly in neurology, because of their fundamental role in electric communication across cell membranes.

During the past two decades, the knowledge of ionic solutions has increased immensely. Various types of interactions exist between the ions in solutions and of these solute-solute and solute-solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding of the nature of the solute and solvent i.e. whether the solute

modifies or distorts the structure of solvent. The nature of solute-solute and solute-solvent interactions has been deduced mainly from thermodynamic properties like partial molar volume, free energy of transfer, heats and volumes of mixing. The volumetric and viscosity behaviour of solutes in solution provide information regarding solute-solute and solute-solvent interactions[2]. The infinite dilution partial molar volumes are, by definition, independent of solute-solute interactions and thus can be used to examine solute-solvent interactions.

The enthalpies and entropies of transfer of electrolytes from water to aqueous mixed solvents show a very complex dependence upon solvent composition. These have generally been discussed in terms of change in solvent-solvent interactions in the bulk of solvent (i.e.solvent structure) brought about by the ions. The results obtained in mixed aqueous systems highlight the importance of solvent-solvent interactions between co-ordinated ions and solvent molecules in hydrogen-bonded media.

Many physico-chemical phenomena like solubilities of electrolytes, rates of chemical reactions, phase separation processes and redox potentials are strongly influenced by the selective solvation of ions in mixed solvents. Some technological applications based on this principle such as electro-deposition metal refining and in high density batteries[3-4] have been suggested. The selective solvation behaviour of few copper (II) salts, viz., copper (II) benzoate, copper (II) formate and copper (II) iodate in water+dimethylformamide (DMF) mixtures have been reported[5].

Accurate aqueous data are needed in many fields besides chemistry including geology, oceanography, and boiler engineering[6] and oil recovery systems. These areas require aqueous data over wide range of temperature, pressure and composition.

Due to the importance in geology, industrial and biological[18] systems, a need has developed for accurate thermodynamic data for transition metal salts in aqueous solutions. In biological systems metals like copper, iron and manganese are required for various purposes, while other metals like nickel and cadmium can poison enzymes by substituting for their required metals. Transition metals are also important in geology because they are components of various minerals, while engineers are interested in their role in corrosion processes. For the sake of convenience of presentation various thermodynamic and transport properties are briefly described as follows:

THERMODYNAMIC PROPERTIES

The dissociation of a salt depends upon dielectric constant, polarity of the solvent and on the lattice energy. The process may be visualized as taking place by dissociation of the crystal lattice in to gaseous ions which are then solvated in the solvents as shown below:

$$C^+A^- \longrightarrow C_g^+ + A_g^- \quad \triangle G_{\text{lattice}} \qquad (1.1)$$

and

$$C_g^+ + A_g^- \longrightarrow C_g^+ + A_g^- \quad \triangle G_{\text{solvation}} \qquad (1.2)$$

Since the free energy of solution, $\triangle G_{sol.}$ is thermodynamically given by the following relation:

$$\triangle G_{sol.} = \triangle G_{solvation} - \triangle G_{lattice} \qquad (1.3)$$

therefore, the free energy of solvation of the ions must be considerably larger in order to overcome the lattice energy. This might possibly qualitatively explain why solubility in water is greater than in non-aqueous solvents. In practice, however, the standard free energy

$$\triangle G^o_{sol.} = -RT \ln K \qquad (1.4)$$

where R is the gas constant, T is the absolute temperature, K is the equilibrium constant for the reaction.

$$MX \longrightarrow M^+ + X^- \qquad (1.5)$$

which afford one of the methods by which free energies of solvation and transfer are derived. Of many theories that have been applied to predict changes in solubility with the solvation of the solvent, the majority are dependent upon changes in the electrostatic properties of the solvent.

The quantitative relation between the solubility of simple salts and the dielectric constant of the solvent was carried out by Bjerrum. Unfortunately the formula proposed by Bjerrum was found to give poor results in the solubility calculations. From these studies, it is apparent, however, that the dielectric constant is not the main determinant of solubility but rather ion-solvation, which depends on the solvent base strength of the hydrogen bonding capability. The thermodynamics of transfer of a pair of gaseous ions into a solvent (solvation) has been widely used to describe the ion-solvent interactions, which take place at infinite dilution. The thermodynamic solvation process in general is represented by the following expression:

$$C^+_g + A^-_g \longrightarrow C^+_{sol.} + A^-_{sol.} \quad \triangle Y^o_{sol.} \qquad (1.6)$$

where C^+A^- is the ion pair and $\triangle Y^o_{sol.}$ represents the change in the thermodynamic function involved. The various thermodynamic properties are described below:

(a) Solvation Enthalpies: Solvation enthalpies are obtained either through a Born-Haber cycle, as the difference between the enthalpy part of the lattice energy and the heats of solution at infinite dilution or from the spectrometric study of ion-solvent interactions in the gas phase.

(b) Solvation Entropies: The various methods for the determination of entropies of solvation have been reviewed by Conway and Bockris.

The entropies of the gaseous ions are calculated from the Sackur-Tetrode equation for mono atomic gases, as given below:

$$\overline{S}^{o}_{g} = R[\ln V + 3/2 \ln T + 3/2 \ln M] + C \qquad (1.7)$$

where M is the atomic weight, V is the molar volume and C is a constant. The entropies of the ions can be obtained from electromotiveforce (e.m.f) measurements and from solubility studies or from Born equation applied to free energies.

The entropy of solvation is given by:

$$\Delta S = \overline{S_2}^{o} - \overline{S_g}^{o} \qquad (1.8)$$

where $\overline{S}_2^{o}$ is the partial molal entropy of the electrolyte and $\overline{S}_g^{o}$ is the standard molal entropy of the gaseous electrolyte.

(c) Gibbs Free Energies: The Gibbs free energy, $\triangle G$, may be obtained from the following thermodynamic relation:

$$\Delta G = \Delta H - T\Delta S$$

where $\triangle H$ is the change in enthalpy, $\triangle S$ is the change in entropy and T is the absolute temperature. But some methods give a direct determination of the free energy of solution. The e.m.f of a cell is directly related to the change in free energy involved in the solvation of ion. In cells which are reversible w.r.t. anions and cations such as amalgam cell:

$$\text{MyHg} \mid \text{MX} \mid \text{AgX} - \text{Ag} \qquad (1.9)$$

the standard free energy of solution of an electrolyte, $\triangle G^{o}_{sol.}$ is obtained directly from the standard electrode potential(E^0) of the cell as given below:

$$-\Delta G^{o}_{sol.} = Z F E^{o} \qquad (1.10)$$

The free energies of transfer may be obtained by using electrochemical cells with transport. This may be realized by combining two amalgam cells in which the electrolyte is not in the same medium, e.g. water and another solvent:

$$\text{Ag-AgX} \mid \text{MX}_{\text{water}} \mid \text{MyHg} \mid \text{MX}_{\text{solvent}} \mid \text{AgX- Ag} \qquad (1.11)$$

the net effect of the cell reaction is the transfer of MX from water to the other solvent. The standard potential of this double cell is given by the difference in the standard potential of the aqueous cell ${}_{w}E^{o}_{MX}$ and the non-aqueous cell ${}_{S}E^{o}_{MX}$. This is by definition known as "medium effect" and may be represented as:

$$In\gamma_0 = \frac{W^{Eo}MX - S^{Eo}MX}{RT} \quad (1.12)$$

(d) Molar volume: The thermodynamic quantity known as the partial molar volume has been proved to be very useful tool in elucidating the interactions occurring in aqueous and non-aqueous solutions. Studies of partial molar volume of electrolytes have been used to examine ion-solvent, ion-ion and solvent-solvent interactions. The partial molar volume of electrolytes at infinite dilution (where ion-ion interactions vanish) are appropriate to study ion-solvent interactions since volume properties are easy to visualize (i.e. geometrically and relatively easy to determine from experimental measurements).

For binary solutions, the use of apparent molar volume, ϕ_v is more convenient. The apparent molar volume of an electrolyte is defined by the relation:

$$\phi_V = \left(\frac{V - n_1 v_1^0}{n_2}\right)_{T,P}$$

Where v is the volume of solution containing n_1 moles of water and n_2 moles of electrolyte and v_1^0 is the molar volume of pure water at a given T, and P ($v_1^0 = M_1/d^0$) where M_1 is the molecular weight of water and d^0 is the density of water).

The apparent molar volume in terms of experimentally measured density (d) and the molecular weight M_1 and M_2 of water and the electrolyte is given by:

$$\phi_v = \frac{1}{n_2}\left(\frac{n_1 M_1 + n_2 M_2}{d}\right) - n_1 v_1^0 \quad (1.13)$$

When the molal concentration scale is used, n_2 = molality (m), and n_1 is equal to the number of moles of water in1000g, so that

$$\phi_v = \frac{1}{m}\left(\frac{1000 + mM_2 - 1000}{d d_0}\right) \quad (1.14)$$

Where d^0 is the density of pure water and d is the density of solution. When the molar concentration scale is used $n_2 = C$, the molarity and equation (1.14) becomes

$$\phi_v = \frac{1000(d^0 - d)}{md\,d_0} + \frac{M_2}{d^0} \quad (1.15)$$

The partial molar volume of electrolyte and water (or any other solvent) can be determined from molarities concentration scale by using the relation:

$$C = \frac{md1000}{1000 + mM_2} \quad (1.16)$$

In order to obtain ϕ_v, it is necessary to measure the density (d) or (d^0-d) i.e., the density difference between the solution and pure solvent. This can be demonstrated by examining the probable error in ϕ_v due to uncertainties in density and concentration.

Differentiating Eq. (1.13) with respect to 'c' at constant d,

Probable error in $$\phi_v = \left(\frac{M_2}{d^0} - \phi_v\right)\frac{\delta C}{C} \qquad (1.17)$$

and differentiating with respect to 'd' at constant 'c'

Probable error in $$\phi_v = -\left(\frac{1000}{C}\right)\frac{\delta d}{d^0} \qquad (1.18)$$

Equations (1.16) and (1.17) demonstrate that in dilute solutions ϕ_v is not seriously influenced by errors in c, however errors in d and d^0 cause a large uncertainity in ϕ_v (e.g. when c=0.01M, 1ppm error in d causes an error of 0.1 cm^3 mol^{-1} in ϕ_v).

The extrapolation of the apparent molar volume of electrolytes to infinite dilution and the expansion of concentration dependence of apparent molar volume have been made by three major equations: the Masson equation[7], the Redlich-Meyer equation[8] and Owen Brinkley equation[9].

Masson found that the apparent molar volume, ϕ_v of electrolyte varies with the square root of the molar concentration and can be represented by linear equation:

$$\phi_v = \phi_v^0 + S_v^* \sqrt{c} \qquad (1.19)$$

Where ϕ_v^0 is the apparent molar volume at infinite dilution and is equal to partial molar volume V_2^0 and S_v^* is the experimental slope varying with electrolyte type and charge.

Redlich and Meyer have suggested the use of following extrapolation equation for a given charge type:

$$\phi_v = \phi_v^0 + S_v^* \sqrt{c} + b_v c \qquad (1.20)$$

Where S_v^* is the theoretical limiting slope and b_v is a deviation constant determined from experimental results.

The Redlich–Meyer extrapolation equation represents the concentration dependence of many1:1 and 2:1 electrolytes in dilute solutions. Recently, Hepler[10] has developed a technique of examining the sign of $[\partial^2\phi_v^0/\partial T^2]$ for various solutes in terms of long-range structure making and breaking capacity of the solutes in aqueous solutions using the general thermodynamic equation.

$$[\partial C_P/\partial p]_T = - [\partial^2 \phi_v^0 / \partial T^2]_P \quad (1.21)$$

On the basis of this equation, it has been deduced that structure-making solutes should have positive values and structure-breaking solutes should have negative values.

TRANSPORT PROPERTIES

The movements of solvent molecules in solutions are reflected in transport properties such as relaxation of dielectric polarization, conductance, viscosity and self diffusion etc. In general the rates of movement molecules decrease if there is an increase in the structure due to increased rigidity and vice versa.

The transport phenomenon arises because any system in non - equilibrium state will always try to approach equilibrium if the intensive state variables are constant at all times and have the same magnitude at all positions in a system. At equilibrium the gradients of the parameters are absent, spontaneous processes do not occur and there is no net exchange of matter between the system and its surroundings. If the system is in a state in which these conditions are not satisfied, the system is said to be in non-equilibrium state.

Many of the transport processes in biology and non – living systems are similar since they obey all the laws of physics. Living systems are the open systems constantly exchanging matter and energy with environment. This exchange is not random, but a highly selective transport of substance and energy. In many biological systems of chemical reactions and flows, there is a resultant coupled flow of certain substances, even against a gradient; such a transport of substance is called active transport.

The transport processes can be classified into two categories as described below :

A. Uncoupled Transport Process ,

B. Coupled Transport Processes

A. UNCOUPLED TRANSPORT PROCESSES

When $L_{ik} = 0$ ($i \neq k$) relation $J = LX$ become $J_i = L_{ii}X_i$. It is a phenomenological representation of several familiar empirical laws involving systems which are in non – equilibrium because of the presence of gradient of temperature, density of macroscopic velocity . They are associated with most familiar examples of transport processes such as heat conduction, diffusion and viscosity etc. For these examples the empirical laws are defined as follows:

(i) Fourier's Law of Heat Conduction : According to this law $q = -\lambda$ grad T

where q is a heat flux resulting from the transfer of heat caused by molecular interactions (pure heat flow) , λ is a coefficient of thermal conductivity and grad T is a gradient of temperature.

(ii) Fick's Law of Diffusion : According to this Law Ji = - D grad Ci

where J_i is flux of chemical species i, C_i is concentration of i and D is the diffusion coefficient and is a characteristic of fluid only.

For the fluid flow through a membrane the equivalence of Fick's Law is D 'Arcy's law:

J_i = k dP/1 where k is known as permeability coefficient, which is a constant in the flux force law resulting from a pressure difference dP across the thickness 1. The coefficient k can be the characteristic of the fluid and the membrane and it differ from D in respect that D is always a characteristic of the fluid only.

(iii) Newton's Law of Viscosity : This can be represented as follows:

$$\pi_{yx} = \eta . \partial U_x/\partial U_y$$

where π_{yx} is a term which represents a momentum flux in the Y direction caused by a fluid flowing in X direction with velocity component U_x and η is a coefficient of shear viscosity.

B. COUPLED TRANSPORT PROCESSES

If a transport process involves two or more forces, the flow J_i will be influenced by other forces X_k ($k \neq i$) as well as its its conjugate force X_i .Such transport processes are called coupled transport processes , thermal diffusion , thermo- molecular pressure difference and electro-kinetic effects are known as transport processes. These processes are briefly described as follows:

(i) Thermal Diffusion: When L_{ik} coefficients in equation J= L X (where J is the flux, X is the force and L is the proportionality constant and is called "transport coefficient") are different from zero, coupled transport phenomenon arises. Thermal diffusion is one of the best known coupled transport processes. If a blub filled with gaseous component at a certain temperature is connected to other gaseous component at different temperature, it is found that the diffusion of both gaseous components depends not only on the concentration gradient but also only the temperature gradient. If the two bulbs are kept originally at the same temperature then the diffusion processes causes temperature difference between the two blubs. This phenomenon is as "Dufour Effect" or Diffusion thermo Effect". If thermal energy flow is represents as J_q and its conjugate gradient as X_q and diffusion flux of species i as Ji and its conjugate gradient as X_i , equation can be written as follows :

$$Jq = L_{qq}X_q + L_{qk} X_k \quad (1.22)$$

$$Ji = L_{iq} X_q + L_{ik} X_{k+} \ (i=1,2\text{------}n) \quad (1.23)$$

If X_k , is the concentration gradient of any component , is zero , then equation 1becomes :

$$Jq = L_{qq}X_q \quad (1.24)$$

This is a form of Fourier's Law of heat conduction. If X_q , which represents the temperature gradient , is zero , equation (1.22) becomes :

$$Jq = \sum_{k=1}^{n} L_{ik} X_k \quad (1.25)$$

This is a form of Fick's law of diffusion. The terms L_{qk} X_k and L_{ik} X_q represent the coupling of heat conduction and diffusion process which results in the phenomena of thermal diffusion process which results in the phenomena of Thermal Diffusion and the Dufour Effect, respectively.

(ii) Thermo- molecular Pressure Difference: The thermo molecular pressure difference is observed experimentally in an apparatus consisting of two large reservoirs I and II connected by a membrane, capillary or an orifice. The reservoirs are maintained at different but constant temperatures T_I and T_{II} and a gas is introduced into the system at a pressure such that means free path of the gas is of the order of the diameter of the capillary. It has been observed that the gas flows from the cold to the hot reservoir till a constant pressure difference is given by the Maxwell's equation given below:

$$P_I / P_{II} = (T_1 / T_{II})^{1/2} \quad (1.26)$$

where P_1 and P_{II} represents the pressures difference in two reservoirs respectively.

(iii) Electro- Kinetic Effects: The electro-kinetic phenomenon is a transport process across a membrane or capillary and is observed when a potential gradient is applied .It arise due to the formation of an electrical double layer at the surface of pores or capillary. According to the thermodynamics of irreversible processes[11] the electro-kinetic effects are described mathematically by the following relations:

$$I = L_{II}\Delta\phi + L_{12}\Delta P \quad (1.27)$$

$$J = L_{2I}\Delta\phi + L_{22}\Delta P \quad (1.28)$$

Where , L_{11} ,L_{12} = L_{21} represent phenomenological coefficients ,I the current flow , J the mass flow , $\Delta\Phi$ and ΔP the potential gradient and pressure gradient respectively across a membrane or capillary. Relations (1.26) and (1.27) show that there are two forces involved in electro-kinetic phenomenon and corresponding to these force there are two fluxes viz; current flux and volume flux. The terms L_{12} ΔP and $L_{2I}\Delta\phi$ represent the coupling of electrical current flow and volume flow respectively.

REVIEW OF LITRATURE

Since the results in mixed aqueous organic systems highlight the importance of solvent-solvent interactions and also of interactions between co-ordinated ions and solvent molecules in hydrogen bonding media, therefore the thermodynamic and transport properties of common electrolytic solutions have been reviewed with a special emphasis on binary aqueous-organic mixtures. For the sake of convenient presentation, the present review has been described under the following headings:

A. Thermodynamic Properties

B. Transport Properties

A. THERMODYNAMIC PROPERTIES

Enthalpies and entropies of transfer of electrolytes from water to aqueous mixed solvents show a very complex dependence upon solvent composition. These have generally been discussed in terms of changes in solvent-solvent interactions in the bulk solvent brought about by the ions.

It is well known that standard thermodynamic quantities of ionic and non-ionic solvents are intimately related with the solvent effect on the physico-chemical properties of the solutes, in general, kinetics and equilibria of reactions involving those solutes in particular. It is also well recognized that composition profiles of transfer Gibbs energies, ΔG^{o}_{tr}, of various solutes in different aqueous ionic[8] and non-ionic co-solvent[12-14] systems are usually monotonic, while those for transfer enthalpies, ΔH^{o}_{tr}, and transfer entropies, $T\Delta S^{o}_{tr}$, of various solutes exhibit extremum with mirror-image relationship to each other[15-18]. It is widely believed that the genesis of the observed mirror image relationship of ΔH^{o}_{tr} and $T\Delta S^{o}_{tr}$ in aqueo-cosolvent systems lies in the involved solute induced perturbations of the three dimensional 3D-structure of the aqueo-cosolvent media, if any, relative to that in water.

It is also well known that hydrophobic or amphiphatic solutes or molecular ions with polar sites induce more water molecules around them to organise in a way similar to clathrate hydrates causing hydrophobic hydration (H_bH)[19-20] and result in a significant increase in Gibb's free energy and decrease in entropy of the system.

Sedlbauer et al.[21] have been determined partial molar volumes at infinite dilution in aqueous solutions of NaCl, NaBr, LiCl and CsBr at temperatures from 550K to 725K. Partial molar volumes at infinite dilution provide a convenient test of theoretical models of aqueous

solutions. In this communication, previously published experimental results of the apparent molar volumes for NaCl, NaBr, LiCl and CsBr at near-critical conditions were extrapolated to infinite dilution. In the temperature range included in this study (550 to 725K), ionic association processes must be considered.

The apparent molal volumes of solutions of $MgCl_2$, $MgBr_2$ and $Mg(NO_3)_2$ have been reported[22] in dioxane+water and glycol+water mixtures at different temperatures. The results have been interpreted in terms of ion-solvent interactions. The ion-solvent interactions are stronger in dioxane+water than glycol+water. The volumes of transfer (ΔV^o_{tr}) from water to mixed solvents have also been calculated. From these values it has been inferred that the structures breaking effect of electrolytes is more in dioxane+water and less in glycol + water.

Sang et al[23] measured densities of glycine, L-alanine, and L-serine in aqueous glucose solutions at T = 298.15K by an oscillating-tube densimeter. Apparent molar volumes and limiting partial molar volumes of each amino acid have been calculated.

Zhao et al.[24] determined apparent molar volumes and standard partial molar volumes of $LiClO_4$ LiBr and three symmetrical tetraalkyl ammonium bromides R_4NBr (R=ethyl, propyl, butyl) at 298.15 K from precise density measurements in solvent mixtures of ethylene carbonate with tetrahydrofuran(THF), acetonitrile(AN), ethylacetate(EA) and dimethoxyethane (DME).

Parmar et.al.[25] determined partial molar volumes of citric acid and tartaric acid in water and binary aqueous mixtures of ethanol (5,10,15,20 and 25% by weight of ethanol) at different temperatures and concentrations from the solution density measurements. The data have been evaluated by using Masson equation and the obtained parameters have been interpreted in terms of solute-solvent interactions. The partial molar volumes vary with temperature as a power series of temperature. Structure making/breaking capacities of the organic acids have been inferred from the sign of $[\partial^2\phi_v{}^o/\partial T^2]_p$, i.e. second derivative of partial molar volume with respect to temperature at constant pressure. Both the organic acids behave as structure breakers in water and water+ethanol.

Safonova et al.[26] determined the densities of tetraalkylammonium bromide, R_4NBr (R= Et, Pr, Bu, Hex, Hep, Oct), solutions in dimethylformamide for the composition range (0.05-0.40 mol-kg^{-1}) at 25^0C. Apparent molar volume and limiting partial molar volumes of the electrolytes have been evaluated.

Parmar and Guleria[27] determined the partial molar volumes of oxalic acid and its salts viz., ammonium oxalate, sodium oxalate and potassium oxalate in binary aqueous mixtures of tetrahydrofuran(THF) [5,10,15 and 20 wt. % of THF] at 298.15K and in 5% (w/w) THF+water at five equidistant temperatures. The data have been evaluated using the Masson

equation and the obtained parameters have been interpreted in terms of solute-solute and solutes-solvent interactions.

Parmar et al.[28] determined partial molar volumes of some divalent transition metal sulphates viz., manganese sulphate, cobalt sulphate, nickel sulphate, copper sulphate, zinc sulphate and magnesium sulphate in the binary aqueous mixtures of diethylene glycol(DEG) (5, 10, 20 and 25 wt. % of DEG) from the solution density measurement at 303.15K, and in 5% (w/w) DEG+water at five equidistant temperatures (298.15 to 318.15K).

Iqbal et al.[29] determined apparent molar volume (V_Φ), partial molar volume (V), solute-solute interaction parameter (S_v), partial molar expansivity (E^o_2) and isobaric thermal expansion coefficient (α_2) of mafenamic acid in six different organic solvents namely, methanol, ehtanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol from the measured solution densities over a temperature range of T= 293.15 and T=313.15 ± 0.1K. The effect of temperature on apparent molar volume and partial molar volume was also determined.

Oswal et al.[30]determined apparent molar volumes of *n*-propylamine, n-butylamine, di-*n*-propylamine, di-*n*-butylamine, triethylamine, tri-*n*-propylamine, and tri-*n*-butylamine in cyclohexane and benzene at 303.15 and 313.15K from the densities ρ determined with high precision vibrating tube densimeter. From these data limiting excess partial molar volumes were estimated. The results were analysed and interpreted in terms of disruption of amine-amine and solute-solvent interactions.

Hynĉica et al.[31] determined density data for dilute aqueous solutions of 1,2-ethanediol(ethylene glycol), 1,2-propanediol, 1,3-propanediol, and 1,2,3-propanetriol were presented together with partial molar volumes at infinite dilution from the experimental data.

R. R. Gupta and Mukhtar Singh[32] determined the apparent molar volumes of oxalic acid in water and in aqueous solutions of sucrose at different temperatures (293.15, 303.15, 313.15 and 323.15K). The density data have been analysed by using Masson's equation. The limiting apparent molar volumes have been used to calculate the partial molar volumes of transfer of oxalic acid from water to aqueous solutions of sucrose. The results have been discussed in terms of various interactions operating in oxalic acid, water and sucrose systems.

Parmar and Attri[33] determined the partial molar volumes of some common tetra-alkyl ammonium and multivalent electrolytes viz., potassium nitrate, ammonium sulphate, tetra-butyl ammonium bromide, tetra-butyl ammonium iodide, ammonium nickel sulphate, ammonium aluminium sulphate, potassium aluminium sulphate and ammonium ceric nitrate in aqueous and binary aqueous solutions of urea (5,10,15,20 and 25 wt.% of urea) from solution density

measurements at 298K, in water and in 5% (w/w) urea+water at four different temperatures. The density data have been analysed by means of Masson's equation.

B TRANSPORT PROPERTIES

(a) TRANSPORT PROPERTIES OF SOLUTIONS

The behaviour of electrolytes in solution is revealed by fundamental transport properties like conductance, viscosity and diffusion etc. These studies help in elucidating the nature of ion-ion and ion-solvent interactions. During the past two decades lot of data has been reported for different types of electrolytes in aqueous medium and binary aqueous mixtures of organic solvents and the same has been summerized as follows:

Viscosities and densities of aqueous solutions of glycine, DL -alanine, DL-α- amino-*n*-butyric acid, DL-valine, DL-leucine and L-serine have been measured[34] as a function of amino acid concentration at 278.15, 288.15, 298.15 and 308.15K. These data have been used to calculate the apparent molar volumes $V_{2,\Phi}$ and viscosity B-coefficients.

The densities and viscosities of ammonium sulphate, sodium sulphate, magnesium sulphate and aluminium sulphate in 40 mass % tetrahydrofuran+water mixture have been measured[35] at temperatures 303, 308, 313 and 318K. Apparent molar volumes (ϕ_v)and viscosity B-coefficients of these electrolytes are derived form these data. The limiting apparent molar volumes (ϕ_v^o) and experimental slopes (S_v^*) obtained from Masson equation have been interpreted in terms of ion-solvent and ion-ion interactions respectively. The viscosity data have been analysed using Jones-Dole equation. The ϕ_v^o values vary with temperature as power series of temperature. The structure making/breaking capacities of the electrolytes studied here have been inferred from the Hepler's criterion.

Parmar et al.[36] determined relative viscosities of some mineral salts viz., sodium sulphate, potassium sulphate, ammonium sulphate and magnesium sulphate at different concentrations in binary aqueous solutions of urea (mole-fractions of urea, X_{urea}= 0.010, 0.025, 0.040, 0.055 and 0.70) at 308.15K and in X_{urea} = 0.025 at different temperatures The data have been evaluated using Jones-Dole equation and the obtained parameters are interpreted in terms of ion-ion and ion-solvent interactions.

Bai and Yan measured[37] viscosity and density data for the system of heptanedioic acid dissolved in aqueous sucrose solution at temp. range from 288.15 to 313.15K. The viscosity B-coefficient for heptanedioic acid in aqueous sucrose solution has been calculated.

Viscosities of ammonium thiocyanates, sodium, potassium, manganese, cobalt, nickel,cadmium sulphates have been measured[38] in water+N,N-dimethylfomamide(DMF) mixtures at 20^0C. The experimental data have been analysed using Jones-Dole equation and the B-coefficients have been calculated. The results have been discussed in terms of ion-solvent and solvent-solvent interactions.

The viscosities of cesium halides (Cl^-, Br^- and I^-), $(C_4 H_9)_4NBr$, NaBr and $NaBPh_4$ have been measured[39] in 0, 20, 40, 80 mass% of aqueous acetone at 298.15K. The viscosity B-coefficient have been determined using the reference electrolyte $NaBPh_4$, NaBr and $(C_4H_9)_4NBr$.

Akhter and Huque[40]measured viscosities and densities of aqueous solution of NaCl and KCl in presence of hydrazine at different temperatures (20^0, 25^0, 30^0, 35^0 and 40^0C). Apparent specific volume (Φ) of the solutions were calculated. The results indicate that with various percentages of hydrazine, NaCl acts as structure maker. At low percentages of hydrazine KCl acts as structure breaker.

Parmar and Thakur[41] determined relative viscosities for the solutions of some divalent transition metal sulphates, viz., manganese sulphate, cobalt sulphate, nickel sulphate, copper sulphate and zinc sulphate and magnesium sulphate at different concentrations in water and in water+ethylene glycol(EG) (5, 10, 15, 20 and 25 % by wt. of EG) mixtures at 303.15K and in water and in 5% (w/w) EG+water at five different temperatures. The data have been analysed using the Jones-Dole equation and the obtained parameters have been interpreted in terms of ion-ion and ion-solvent interactions.

The standard partial molar volumes, viscosity B-coefficients and activation free energies of lithium salts ($LiClO_4$ and LiBr) in propylene carbonate(PC) with 1,2-dimethoxyethane(DME) mixed solvents have been determined[42] as a function of the mole fraction of DME at 298.15K from precise density and viscosity measurements. The values studied are all positive and decrease monotonously with addition of DME in the PC, which indicates that nature of the solvents plays an important role. The effects are discussed in terms of preferential salvation and packing effect in the salvation shell and electrostriction. The differences between ClO_4^- and Br^- have also been discussed.

Densities ρ and viscosities η of two hydroxamic acids, N-phenyl-2-chlorobenzo- and N-*o*-tolyl-4-chlorobenzo-, have been determined[43] as a function of their concentration in aqueous acetone solution at temperatures 303.15 and 313.15K. Apparent molar volumes, standard-state partial molar volumes and relative viscosities have been calculated. The viscosity data have been analysed using Jones-Dole equation. The activation thermodynamic parameters of viscous flow have been evaluated usig Feakins equation.

Daabes and Awwad[44] were measured densities, ρ, and viscosities, η, of aqueous solutions of N-(2-hydroxyethyl) morpholine over the entire composition range at T = (293.15, 303.15, 313.15, 323.15, 333.15)K and at atmospheric pressure. The excess molar volumes V^E and viscosity deviations η^E of aqueous solutions were calculated from the experimental results of density and viscosity measurements and fitted to the Redlich–Kister polynomial equation. Apparent molar volumes V_Φ, partial molar volume at infinite dilution V^∞, and the thermal expansion coefficient were also calculated.

Densities of binary mixtures of N-(2-hydroxyethyl) morpholine with ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol were measured[41] over the entire composition range at temperatures from (293.15 to 323.15)K and atmospheric pressure using a vibrating-tube densimeter. The excess molar volumes, V^E were calculated from density data and fitted to the Redlich-Kister polynomial equation. Apparent molar volumes, partial molar volume at infinite dilution and the thermal expansion coefficient of the mixtures were also calculated. The V^E values were found to be negative over the entire composition range and at all temperatures studied and become less negative with increasing carbon chain length of the alkanol.

Sinha et al.[45] determined apparent molar volumes and viscosity B-coefficients for nicotinamide in (0.00, 0.05, 0.10, and 0.15) mol. dm^{-3} in aqueous tetrabutylammonium bromide(TBAB) solutions from solution density and viscosity measurements at temperaturs over the range (298.15 to 318.15K as a function of concentration of nicotinamide(NA).

Dubey and Coworkers[46] have been measured densities and speeds of sound over the whole composition range for (butan-1-ol with hexane, or octane, or decane) at T= (298.15, 303.15, and 308.15)K and atmospheric pressure along with the properties of the pure components.Viscosities (η) of these binary mixtures have also been measured over the entire composition range at T= 298.15K. Experimental values of density, viscosity and speed of sound have been used to evaluate excess properties viz., excess molar volumes (V^E), deviation in viscoisty (Δη), deviation in speeds of sound (Δu), deviation in isentropic compressibility (Δ_{Ks}) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}).

(b) TRANSPORT PHENOMENON ACROSS MEMBRANES

Thermodynamics of irreversible processes has been applied for the study of transport phenomenon across different type of diaphragms involving electrolytic and non electrolytic

solutions both theoretically and experimentally by number of workers during the recent past, and a brief account is given below.

The phenomenological permeation coefficients have been determined for two artificial cellulose membranes of known thickness and water content. Transport of non- electrolytes were studies withed tagged water, urea, glucose and sucrose. The effect of the unstirred layers on the experimental determination of the coefficients has been discussed. Frictional coefficients between membrane matrix and solute and between solvent and solute on the matrix are calculated It has been shown that the geometrical tortuosity does not correspond to a physical tortuosity.

The hydrodynamic permeabilities of aqueous solutions of ueara , glucose and their liquid mixtures across urinary bladder of goat has been studied by Shukla and Misra [47].In urea-glucose mixtures , with increasing urea concentration at constant glucose concentration , the hydrodynamic permeability first increases and then decrease. While in case of glucose – urea mixtures, permeability first decreases and then increases with increasing glucose concentration at constant urea concentration. The membrane has been found to be anisotropic.

Blokhra et.al.[48] have reported the transport of urea and thiourea across a cation exchange membrane , prepared by the mechanical treatment , using araldite as a binder. The membrane so formed has been characterized in terms of pore radius, number of pores and zeta potential developed across the membrane during transport.

Blokhra et.al. [49] have also employed methanol + water mixtures as permeant through a chemically treated oakwood membrane . The variation of coefficient L_{ki} and L_{ik} with the mass fraction of the methanol was non linear. These trends were attributed to the structural modification which occur in water + methanol mixtures due to hydrogen bonding.

Parmar and Sidhu[50] have studied the permeability of water and aqueous solutions of urea ,ferrous sulphate and zinc sulphate through a soil membrane . Permeability coefficients (L_p) have been calculated for water and different fluids .At lower concentration ($\leq$ 0.01 M), the L_p values vary in following order :Urea > $FeSO_4$ > $ZnSO_4$ >H_2O whereas at higher concentration , L_p varies as follows :$FeSO_4$ > $ZnSO_4$ > Urea > H_2O.The results indicate that the interaction between soil and urea solution increases with increase of urea content whereas in case of $FeSO_4$ and $ZnSO_4$ the interactions go on decreasing. The equivalent pore radius of soil membrane varies with concentration of solute which is attributed to change in electrical double layer at the solution – soil interface.

Parmar and Soni [51] have studied the hydraulic permeability of water and aqueous solutions of some sulphates viz ; $(NH_4)_2SO_4$, $MgSO_4$ and K_2SO_4 across a soil membrane of

known thickness at 30^0C.The permeability coefficient , L_p , has been found to be minimum for water and maximum forpotassium sulphate. The dependence of the frictional coefficient (f_{wm}) between soil matrix and water, and equivalent pore radius of soil membrane on concentration of sulphate has also been discussed.

OBJECTIVE OF PRESENT STUDIES

The behaviour of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interactions in general are stronger than the latter. Ion-Ion interaction in dilute electrolyte solution is now well understood theoretically but the ion-solvent interaction (ion-solvation) still remains complex process. The survey of literature showed that although many studies on thermodynamic and transport properties (already discussed in the literature) have been carried out both in single component and mixed solvent systems but a little attention has been paid to the behaviour of transition metal chlorides and magnesium chloride in water and water+ monohydroxy alcohols.

Survey of literature also showed that many studies on thermodynamic and transport properties of electrolytes have been carried out both in pure as well as in mixed solvent systems but a little attention has been paid to the behavior of transition metal chlorides and magnesium chloride in mixed solvent systems.

The mixed solvents systems are used in a wide range of applications and understanding the effects of changes in solvent composition remains a central problem within physical chemistry. During recent years there has been an increasing interest in the study of the behavior of electrolytes in mixed solvents, because the use of mixed solvents enables to know about the nature of ion – ion and ion – solvent interactions under the varied conditions simply by changing the solvent composition. The study of thermodynamic and transport properties of these electrolytic solution provides an opportunity for extending the range of properties from which the structure of electrolyte solution can be inferred.

It has been realized that ion – solvation interactions play an important role in the solution chemistry. Most of such studies have been carried out in water (w), which is a structured solvent par excellence. If the nature of w can be modified by a co – solvent in such a way that the electrostatic effects, arising from dielectric constant remain almost the same , then the chemical effects of the co – solvent should play an important role in influencing ion – ion interactions.

Moreover, mixed binary aqueous solvent systems behave in unexpected systems. These observations have given a new impetus to the detailed study of structure of binary aqueous mixtures. The information drawn from the studies of thermodynamic and transport properties have been related to structural aspect of the solvent in terms of ion – solvent interactions and structure making/breaking capacity of various electrolytes.

Scientists and engineers working in various disciplines of science and technology are getting interested in studies on transport processes and the biologists are

taking more and more interest in these studies, since most of the biological processes are the transport processes. The survey of literature shows that the transport phenomena, involving transition metal salts, across inorganic membranes have not been reported so far, even in binary systems , what to talk of ternary systems. So in the present investigation an inorganic membrane shall be utilized because some of the inorganic membranes have been considerably used in the conversion of sea water to fresh water and in the fuel cells. The studies on the membranes of inorganic ion-exchangers are more stable than the membranes of organic materials.

Since the results in mixed aqueous organic systems highlight the importance of solvent – solvent interactions and also of interactions between co-ordinate ions and solvent molecules in H – bonding media , therefore the main objectives of the present study will be to investigate the thermodynamic property viz; partial molar volume and transport processes such as viscous flow and permabilities of some divalent transition metal chloride and magnesium chloride in binary aqueous mixtures of alcohols with or without inorganic membrane.

The main objectives of the present investigations are:

(i) To estimate the partial molar volumes of some transition metal chlorides such as manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water and binary aqueous mixtures of alcohols.

(ii) To test the various theories used for describing the uncoupled transport property viz ; viscous flow of some transition metal chlorides and magnesium chloride (mentioned above) in water and binary aqueous mixtures of alcohols at various temperatures .

(iii) To investigate the coupled transport phenomenon viz ; hydrodynamic permeabilities of manganese chloride, cobalt chloride, nickel chloride ,copper chloride, cadmium chloride and magnesium chloride in water and binary aqueous solutions of alcohols across an inorganic membrane of aluminum oxide.

DESCRIPTION OF PROPOSED WORK

The thermodynamic quantity known as partial molar volumes of transition metal chlorides such as manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride will be measured in water and binary aqueous solutions of alcohol at various compositions and different temperatures.

The partial molar volume of solutes at infinite dilution will be calculated by the Masson equation:

$\phi_v = \phi_v^0 + S_v^* \sqrt{c}$ Where ϕ_v : partial molar volume

ϕ_v^0: partial molar volume at infinite dilution (ion-solvent interactions)

S_v^*: experimental slope (ion-ion interactions)

Also we will study the effect of temperature on apparent molar volumes of these transition metal chlorides in water as well as in binary aqueous solutions of alcohol to examine the structure making /breaking behavior of these electrolytes in water and binary aqueous systems.

Hepler has developed a technique of examining the structure making and breaking behavior of different electrolytes.

$$[\partial C_P/\partial p]_T = - [\partial^2 \phi_v^0 / \partial T^2]_P$$

On the basis of this equation, it has been deduced that structure-making solutes should have positive values and structure-breaking solutes should have negative values.

The transport phenomenon viz., viscous flow of transition metal chlorides in aqueous and binary aqueous solutions of alcohol shall be described.

The study of viscosity lead to the information about displacement of equilibrium positions of molecules. It has been found by the no. of workers that the addition of an electrolyte or solute either breaks or makes the structure of a liquid.

The viscosity of electrolytic or non-electrolytic solutions is usually interpreted in terms of Jones-Dole equation.

$\eta_{rel} = \eta/\eta_0 = 1+Ac^{½} + Bc$

Where η_{rel} :relative viscosity of solution

A :(ion-ion interactions) positive computable constant

B : (ion-solvent interactions)empirical constant

C: molar concentration

The negative B-coefficient implies a decrease in velocity in the presence of a solute and hence increases in the fluidity which results into the net decrease in the structure of the solvent.

Conversely, an increase in the structure increases the rigidity and hence the viscosity of the solvent resulting in a positive B-coefficient.

But it is usually difficult to separate the ionic size effect from the structural effect of B-coefficient, the better criteria for solvent structural influence would be the temperature dependence of the B-coefficient i.e. dB/dT. According to this criteria, structure breaker solutes have positive values of dB/dT, while the structure makers have negative value.

Recently lot of data on viscosity have been reported in water and some hydrogen bonded solvents and binary mixtures of aqueous-organic solvents for different types of solutes but data for transition metal chlorides is extremely less and in particular no data have been noticed for such types of solutes in binary aqueous solutions of alcohols. Therefore there is no reason for not trying a comparative study of transition metal chlorides in binary aqueous solution of alcohols.

We will measure the hydrodynamic permeability, electro-osmotic velocity ,electro-osmotic pressure and streaming potential for different aqueous solutions of some transition metal chlorides across membrane at different temperatures. Permeability coefficient L_p ,will be determined as a function of hydrodynamic pressure and concentration of solute. Coupling coefficient σ ,as a function of solute concentration will also be determined and in last to know the mechanism of flow across the membrane of alumina activation parameters will also be determined.

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EXPERIMENTAL DETAILS AND METHODOLOGY

The experimental details and methodology is described as follow:

- **A.** Materials
- **B.** Preparation of solution
- **C.** Determination of density
- **D.** Determination of viscosity
- **E.** Measurement of hydrodynamic permeabilities

A. MATERIALS

(a) Conductivity water : The water used for study will be obtained by distilling the water twice over alkaline $KMnO_4$ and $K_2Cr_2O_7$ in glass apparatus using long fractionating column. The specific conductance of water must be of the order of 10^{-6} $Ohm^{-1}cm^{-1}$.

(b) Reagents: The reagents magnesium chloride [$MgCl_2.6H_2O$, M. W. 203.30 g], manganese chloride [$MnCl_2$. $4H_2O$, M.W. 197.9 g], nickel chloride [$NiCl_2.6H_2O$, M.W.237.71 g] ,copper chloride [$CuCl_2.2H_2O$,M.W.170.48 g], cobalt chloride [$CoCl_2.6H_2O$,M.W. 237.93 g],cadmium chloride [$CdCl_2.H_2O$.M.W.201.32] and mono hydroxy alcohols (Metahnol and Ethanol) of AR grade will be taken.

B. PREPARATION OF SOLUTION

The different compositions of monohydroxy alcohol-water and solutions of the electrolytes will be prepared by weight. The molality (m) of electrolyte solution will be converted into molarity(c) by using the following expression:

$$C = \frac{d.m.1000}{1000+mM_2} \qquad (2.1)$$

where d is the density of electrolyte solution, and M_2 is molecular weight of electrolyte.

C. DETERMINATION OF DENSITY

The density will be measured with the help of apparatus shown in fig. I similar to the one described by ward and millero[1]. 'A' is a glass float which is suspended from balance pan'G' with the help of a nylon thread 'H' into a cylindrical sample container 'B' of 250 ml capacity. The sample container has bakelite top 'F' with a hole in the centre for nylon thread to pass through. The sample container will be placed in water-bath 'E', 'C' is stirrer and 'D' is thermometer. The whole assembly of sample container and water-bath will be placed in thermo-stat whose temperature was controlled with the help of an electronic relay. The fluctuation in temperature should be within $\pm$ 0.01^0C. The sample container and glass float will be thoroughly cleaned by washing them with chromic acid first and finally with acetone. The volume of float will determined with the help of following equation :

$$V_f = \frac{w_{air} - w_{water}}{d_o} \qquad (2.2)$$

where W_{air} is weight of float in air and W_{water} is weight of float in water and d_o is density of water at a particular temperature T. To obtain the W_{water} the sample container will be filled with water (after suspension of float in it) so that level of water came upto fixed mark on the container.

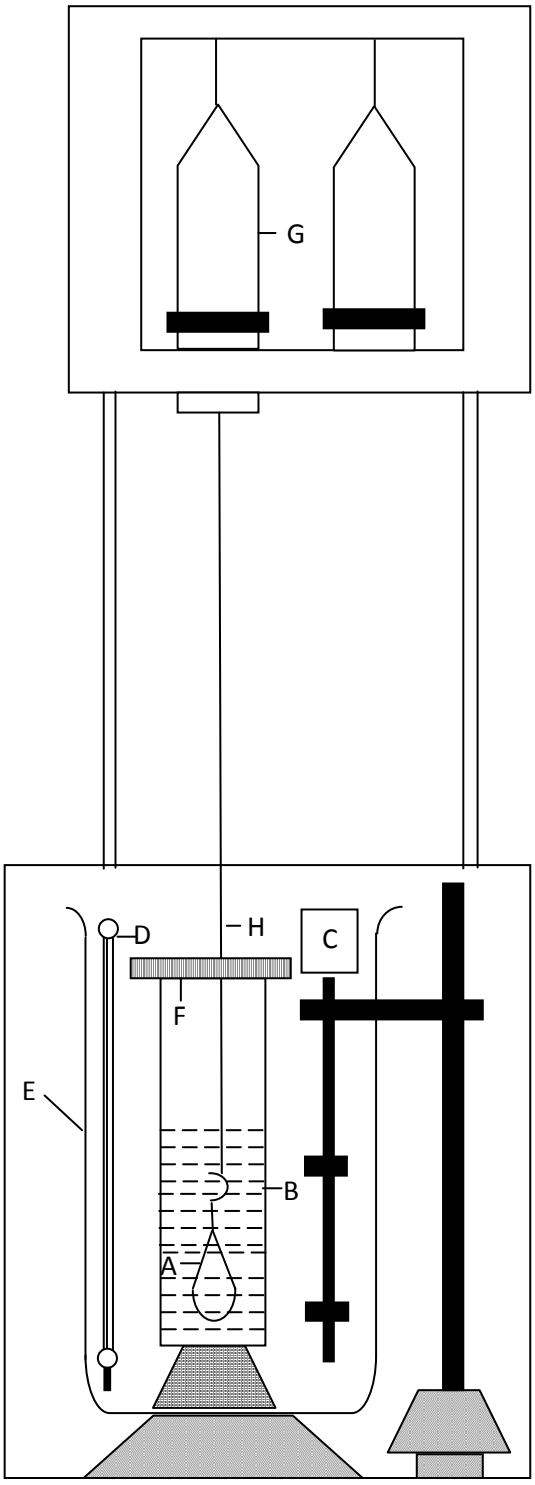

Fig.1: APPARATUS FOR MEASUREMENT OF DENSITY

In the present studies a 37.036 g float of volume 33.138 ± 0.057 cm^3 at 303.15K was used. The density of solution was calculated using the relationship.

$$d - d^0 = \frac{w_o - w}{v_f} \quad (2.3)$$

where d is the density of solution under study and d_o is density of pure solvent at particular temperature, W is weight of float in solution (under study) and W_o is the weight of float in pure water, V_f is the volume of float. While performing experiment every care will taken so that suspension thread do not touch any part of equipment. The calibration of float will be checked by measuring density of some liquid whose literature value is known.

D. MEASUREMENT of VISCOSITY

Viscosity measurements will be made with the help of suspended level type viscometer. Runs will be repeat until three successive determinations will obtained within ±0.01 second. The viscometer, shown in Fig.2 consists of a U-tube with two bulbs D and E, along with a side arm F. The left hand limb is essentially a pipette with two definite marks A and B above and below the bulb D and a capillary about 10" long. Some volume of solution is introduced into the bulb E. Keeping the side arm, 'F', closed, the solution will forced through capillary tube C until the meniscus stood above the mark A. On opening the side arm, F, while keeping the capillary limb closed, the solution below C fall back and the column of the solution CA is held suspended. On opening the capillary limb the solution flows through the capillary and the time of flow of meniscus from A to B will be noted.

The viscometer will be clean by filling it with chromic acid, followed by washing with water and finally with acetone. The viscometer will dried by applying vacuum. Flow time for volume of solution through the capillary, between the marks A and B will be measure with the help of a stop watch capable of recording time upto 0.01 second. Viscosities of solutions will determine at different temperatures in water thermostat controlled upto $\pm 0.01^0$C by means of an electronic relay and contact thermometer. Time of flow (for solution in bulb) between marks A and B will be determined by visual observation. The density measurements needs for calculations of viscosity will be made as described in section(C). The relative viscosities of solutions will be obtained by using following equation :

$$\eta_r = \frac{\eta}{\eta_o} = \frac{dt}{d_o t_o} \quad (2.4)$$

where η and η_o are the viscosities of solution and solvent respectively, η_r is the relative viscosity, d and d_o are the densities of solution and solvent respectively, t and t_o are therespective flow times.

In order to determine the hydrodynamic permeability, electro-osmotic velocity ,electro-osmotic pressure and streaming potential for different aqueous solutions of some transition metal chlorides across membrane at different temperatures following experimental procedure and methodology will be followed .

(i) Preparation of the membrane
(ii) The apparatus
(iii) The experimental procedure

(i) Preparation of the membrane: The aluminum oxide will be swollen in conductivity water and casted in the form of a plug as described below:
10.00 g of swollen material along with small amount (about 5-6%) of an adhesive (araldite) will be placed in a pyrex glass tube having a constriction in the middle and compressed mechanically at the site of construction with the help of a mechanical device shown in fig: 3.It will be left as such for about 24 hours for the complete setting of the plug. The thickness and diameter of the plug will be measured. The maximum variation in the permeability of aluminium oxide membrane thus prepared after one week will be only the order of 5%.
In order to know the directional character of the membrane for the permeation of water, the flow /hydraulic permeability will be measured in both the direction at 298K and the values should be the same in both the directions thereby indicating the isotropic character of the membrane.

(ii) Apparatus: The design of the apparatus and its experimental set up is shown in fig. 4 The apparatus consists of a pyrex glass tube of 29 cm in length having a slight construction in the middle with an internal diameter 1.858 cm where the plug of aluminum oxide is set up. This tube has two standard female joints B-24 at the ends. To the standard B-24 male joints are fixed the coiled platinum electrodes F and G .The ends of the electrodes are fused in glass tubes of diagram 5 mm ,so that the electrode ends are insulated from the permeant. The length of these glass tubes are adjusted in such a way that when standard joints are kept in position, the

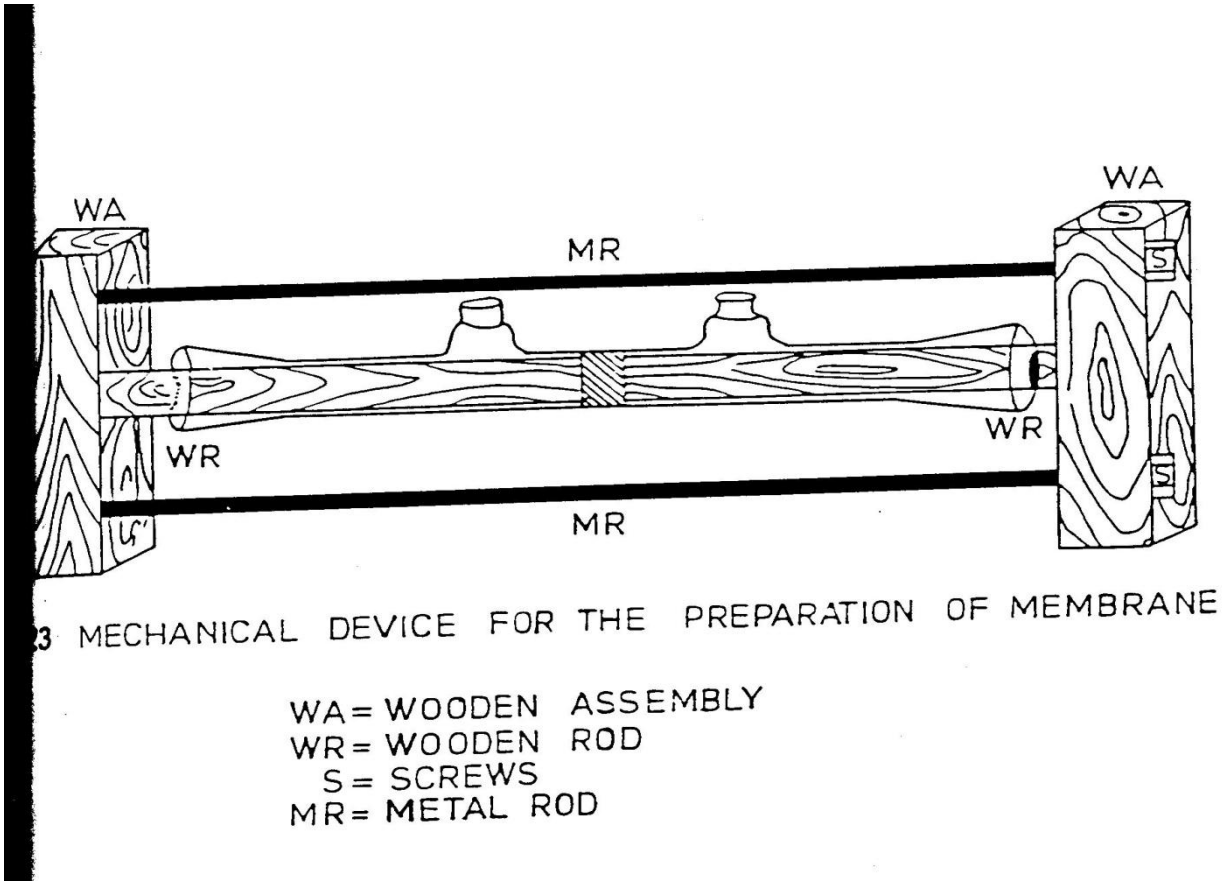

Fig 3: MECHANICAL DEVICE FOR THE PREPARATION OF MEMBRANE

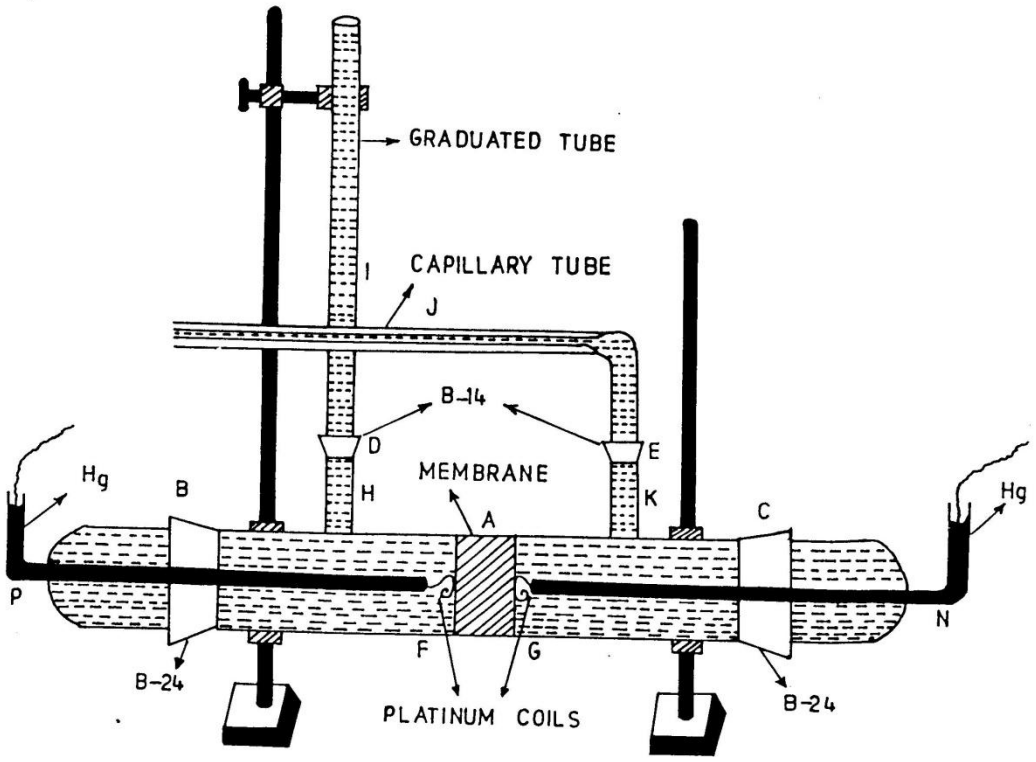

FIG. 4: SCHEMATIC SET UP OF THE APPARATURS

electrodes touch the cross-sectional surface of the membrane .The main tube has two sides tubes H and K, bearing B-14 female standard joints D and E.Through the joint E a capillary tube, J, of length 19 cm and diameter 0.16 cm bent at 90^0 is connected to the side tube K. A graduated tube I of length about 50 cm and 1.0 cm in diameter is connected to the sides tube H through another standard joint D.

(iii)The Experimental Procedure: The experimental cell will be filled with water and left overnight for equilibration of the membrane. The cell will be then thoroughly washed with fresh distilled water under pressure gradient to ensure the thorough cleanliness. The apparatus will be filled by adding conductivity water on one side of the membrane and then sucking it to the other sided under a pressure gradient by mean of a vacuum pump. This ensured the complete filling of

the capillaries of the membrane. Thus tubes J and I would then introduced and the apparatus suitably mounted inside the thermostat, where it will be allowed to attain a constant temperature. The temperature will be adjusted with the help of a contact thermometer and an an electronic relay. To make the contacts with electrodes, mercury will be added into the tubes P and N. In order to measure the hydrodynamic permeability, desired pressure difference was introduced across one side of the cell with the help of a pressure head. The system will be kept in the thermostat for about two hours to allow the experimental solution to attain the temperature of the thermostat. The rate of flow of liquid at desired pressure difference will be measured by noting the time as taken by the solution to move a certain distance through horizontal capillary. The flow time will be recorded with the help of a stop of least count 0.01 second. In this way the flow was recorded at different pressures.

For measurement of coupling coefficient (σ) one chamber of the apparatus will be filled with a particular solution of the solute and other chamber with pure solvent.A desired pressure head of solvent will be then applied on the side of the solvent chamber and the capillary will be attached on the side of solution to note the net (resultant) volume flow, J_v. The value of L_p' and J_v' were calculated from the slope and intercept of the plot of J_v' vs p' respectively.
Conductance of the system (membrane + solution) and specific conductance of the solution will also be noted with the help of a digital conductivity bridge.

Permeability coefficient L_p , will be determined as a function of hydrodynamic pressure and concentration of solute. Coupling coefficient σ , as a function of solute concentration will also be determined and in last to know the mechanism of flow across the membrane of alumina activation parameters will also be determined.

REFERENCES

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